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HARFMFUL INSECT CONTROL AGENT FOR CLOTHES AND A STORAGE
FANUTURE MEMBER
[IRUIYO GAICHU BOJYOZAI OYOBİ SHUNOKAGU BUZAI]

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UNITED STATES PATENT AND TRADEMARK OFFICE
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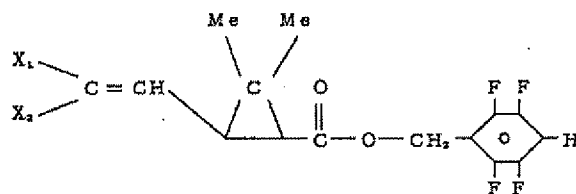
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| TITLE | (54) : | HARMFUL INSECT CONTROL AGENT FOR CLOTHES AND A STORAGE FURNITURE MEMBER |
| FOREIGN TITLE | [54A] : | IRUIYO GAICHU BOJYOZAI OYOBI SHUNOKAGU BUZAI |

Claim(s)

1. An insect control agent for clothes, which is featured by containing a compound expressed by the following chemical formula (1):

Formula (1)

[Chemical Formula 1]



(where X_1 and X_2 are chlorine and/or a methyl group).

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a so-called "harmful insect control agent for clothes", and more specifically relates to a harmful insect control agent for clothes, which is effective for long period and is safe.

[0002]

[Conventional Technique]

Conventionally, for a harmful insect control agent for clothes, a control agent, such as p-dichlorobenzene, naphthalene, and camphor, has been widely used. These agents are to protect clothes by their subliming vapor by

placing near clothes. Major effect of those insect control agents, however, is originally to repel harmful insects, and has characteristic odor. Therefore, this odor causes odor transfer to clothes stored near the agents and generates uncomfortable feeling upon wearing, which is an issue to be solved in an insect control agent for clothes. Therefore, it has been recently studied to search for an insect control agent that is odor free and is effective by small amount.

[0003]

For an insect control agent that satisfies those conditions, only 1-ethynyl-2-methyl-2-pentenyl chrysanthemate (hereinafter referred to as "empenthrin") is known. Although this agent has high insecticidal activity against harmful insects, it hardly keeps the effect for long period. For use, every sort of slow-releasing methods (e.g. Unexamined Japan Patent Application Publication H2-196704) has been disclosed.

[0004]

On the other hand, Unexamined Japan Patent Application Publication S63-203649 discloses 2,3,5,6-tetrafluorobenzyl (+) 1R,3S-trans-2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane carboxylate as a pirethroid insecticide. This agent is shown to be suitable for controlling a harmful

animal as a hygienically harmful living organism or a harmful living organism for stored products, which are generated in household, especially an insect. For a harmful living organism, *Lepisma saccharina* for the order Thsanura; *Blatta orientalis*, *Periplaneta Americana*, *Leucophaea adela*, *Blattella germanica*, and *Acheta domestica* for the order Orthoptera; *Forficula Anisolabis* for earwigs; *Reticulitermes* for termites; *Pediculus humanus* for lice; *Cimex lectularius* Linnaeus, *Rhodnius prolixus*, and *Triatoma infectans* for the order Hemiptera; *Ephestia kuehniella* zeller and *Galleria mellonella* for the order Lepidoptera, *Anobium punctatum*, *Rhizopertha dominica*, *Hylotrupes bajulus*, *Oryzaephilus surinamensis*, *Sitophilus zeamais* Motschulsky, *Trogoderma* spp., *Anthrenus* spp., *Lyctus* spp., *Niptus hololeucus*, *Gibbium psyllodes*, and *Tribolium* spp. for the order Coleoptera; *Monomorium pharaonis*, *Lasius niger*, and *Vespa* for the order Hemenoptera; *Aedes aegypti*, *Anopheles* spp., *Culex* spp., *Musca* spp., *Fannia* spp., *Calliphora* spp., *Lucilia* spp., *Chrysomya* spp., *Stomoxys* spp., and *Tabanus* spp. for the order Diptera, *Xenopsylla* and *Ceratophyllus* spp. for the order Shiphonaptera are listed. However, effects against clothes moth and webbing clothes moth of the family Tineidae have not been known.

[0005]

[Problems to be Solved by the Invention]

For a harmful insect control agent for clothes, while it is required to have strong insect control effect against harmful insects for clothes and an insect damage preventing effect, it is also required to have low toxicity and last the above-described effects for long period. However, conventionally known harmful insect control agents for clothes, such as p-dichlorobenzene, naphthalene, and camphor, are inexpensive, and a large amount of them is used to make the effects last for long period. Accordingly, the toxicity is higher, and the effects are not satisfactory.

[0006]

On the other hand, a pirethroid compound, which has been known as a general insecticide for household use against flies, mosquitoes, and so on, has low toxicity. Especially empenethrin has been already used as a harmful insect control agent for clothes, but requires troublesome treatments for slow releasing, such as encapsulating in resin or a microcapsule, etc., which makes the agent expensive.

[0007]

For this reason, it has been demanded to find a compound that is effective for long period and has low toxicity and develop an effective harmful insect control agent for clothes.

[0008]

It is an object of the invention to provide a pirethroid-based harmful insect control agent for clothes, which exhibits superior insect control effect against harmful insects, especially clothes moth and webbing clothes moth, etc., and can keep the effects for long period.

[0009]

[Means to Solve the Problems]

Inventors of this invention conducted thorough studies on an insect control effect of a number of pirethroid compounds, especially compounds known as pirethroid insecticides, against clothes moth and webbing clothes moth, which are representatives of harmful insects for clothes, and completed the invention.

[0010]

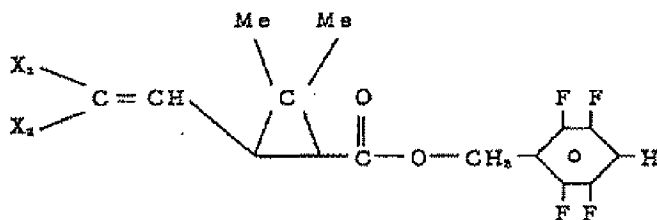
More specifically, the present invention is a harmful insect control agent for clothes, which is featured by containing as an active ingredient a compound generally

expressed by the following chemical formula (1), and achieved the above object:

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Formula (1)

[Chemical Formula 2]



(where X₁ and X₂ are chlorine and/or a methyl group.)

[0011]

In the compound, which is an active ingredient of the harmful insect control agent for clothes according to the invention and is generally expressed by the chemical formula (1), any of X₁ and X₂ can be chlorines or methyl groups, or one of them can be chlorine and the other can be a methyl group, and even one of those compounds has many enantiomers and geometric isomers. Among them, 2,3,5,6-tetrafluorobenzyl (+)1R,3S-trans-2,2-dimethyl-3(2,2-dichlorovinyl)-cyclopropane carbonate (hereinafter, referred to as "Compound (1)") is preferred. In addition, 2,3,5,6-tetrafluorobenzyl (-)1R,cis/trans-2,2-dimethyl-3(2,2-dichlorovinyl)-cyclopropane carbonate and 2,3,5,6-

tetrafluorobenzyl (±)1R,S-cis/trans-2,2-dimethyl-3(2-methyl-1-propenyl)-cyclopropane carbonate (hereinafter, referred to as "Compound (2)) can be also used.

[0012]

The harmful insect control agent for clothes according to this invention can exhibit superior control effect against harmful insects for clothes, and the active ingredient has appropriate vapor pressure, i.e. 2.7×10^{-4} mmHg/25 °C (obtained by extrapolation), which is almost halfway between vapor pressure of conventional highly subliming pirethroid compounds (normally on the order of $\times 10^{-3}$ mmHg/30 °C) and vapor pressure of common pirethroid compounds (normally on the order of $\times 10^{-5}$ mmHg/30 °C). Therefore, it can be fully expected to exhibit the gasifying effect and lasting effect at normal temperature, and has extraordinary performances such as substantially odor free and extremely low toxicity. Especially for the effective insect control concentration of the insect control agent according to this invention is, as in later-described test examples, base material impregnated in almost same amount of the agent as that of empenethrin that is already used as a harmful insect agent for clothes is more effective than empenethrin. Accordingly, it is more

effective against harmful insects for clothes such as clothes moth and webbing clothes moth than empenethrin.

[0013]

Therefore, the harmful insect control agent for clothes according to this invention can exhibit satisfactory control effect by smaller amount than empenethrin, and can extend the active period at similar amount.

[0014]

In case of the harmful insect control agent according to this invention, the active ingredient compound can be also applied to a place where the agent is required to exhibit the insect control effects as is, for example, every sort of storage furniture used for storing clothes, such as Japanese-style chest, drawers, ordinary chest, and clothes box. However, it is normally prepared, for example, in solid form, such as powder, granule, tablet, stick, or sheet, or in liquid form, such as emulsifying agent, dispersant, aerosol agent, and oil solution, using suitable carrier or excipient, and applied for controlling harmful insects for clothes by an appropriate method depending on the form of the agent.

[0015]

For the carrier (diluent) used for preparing the agent for liquid form, for example, water, alcohols such as ethyl alcohol, esters such as ethyl acetate, halogenated hydrocarbons such as dichloroethane, ketones such as acetone or methyl ethyl ketone, ethers such as tetrahydrofuran or dioxane, aliphatic hydrocarbons such as hexane, kerosene, paraffin, petroleum benzine, and aromatic hydrocarbons such as benzene and toluene can be used. In addition, for the liquid agent, common emulsifier, dispersant, spreading agent, wetting agent, stabilizer, spraying agent, and so on can be added/compounded. Furthermore, by compounding a normal film-forming agent, it can be made in a form of coating material, adhesive, and so on. For each additive used herein, for example, every sort of film-forming agents, such as cellulose derivatives such as nitrocellulose, acetyl cellulose, methyl cellulose, and acetyl butyl cellulose, vinyl resin such as vinyl acetate resin, alkyd resin, urea resin, epoxy resin, polyester resin, urethane resin, silicone resin, acrylic resin, rubber such as chlorinated rubber, and polyvinyl alcohol; surfactants such as ether of polyoxyethylene fatty alcohol such as polyoxyethylene oleyl ether, polyoxyethylene alkyl allyl ether such as [polyoxyethylene nonylphenyl ether,

ester of polyoxyethylene fatty acid, glyceride of fatty acid, sorbitan ester of fatty acid, sulfate ester of higher alcohol, alkyl allyl sulfonate salt such as sodium dodecylbenzene sulfonate; a spraying agent such as dimethyl ether or fluorocarbon; casein, gelatin, alginic acid, and carboxymethylcellulose (CMC) can be listed.

[0016]

In addition, for a carrier used for preparing the agent in solid form, for a representative example, every sort of mineral substance powder such as silicic acid, kaolin, activated carbon, talc, calcium carbonate, and ceramic powder, every sort of vegetable substance powder such as wood powder, bean powder, flour, and starch, an inclusion compound such as cyclodextrin, and so on can be listed. Furthermore, for preparing the agent in a solid form, for example, using a subliming carrier, such as tricyclodecane, cyclododecane, 2,4,6-triisopropyl-1,3,5-trioxane, trioxane, trimethylene norbornene, p-dichlorobenzene, naphthalene, and camphor, the carrier and the active ingredient compound can be mixed in melted condition or mixed in ground condition, and then can be molded to a subliming solid agent. In addition, the above-described solid agent can also include a form of a resin

molded product, in which the active ingredient compound is kneaded in plastic.

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[0017]

Furthermore, the harmful insect control agent for clothes according to this invention can be also prepared as in a micro-encapsulated form by a spray-dry method using polyvinyl alcohol, CMC, and so on, a hardening-in liquid method using gelatin, polyvinyl alcohol, alginic acid, and so on, or by coacervation method. In addition, it can be also included with cyclodextrin, or prepared in form of gel using gelating agent such as benzylidene-D-sorbitol and carrageenan.

[0018]

The insect control agent for clothes according to this invention, which is prepared in this way, can be any, and suitably determined according to each form, but normally contains the active ingredient compound preferably up to about 80 % (by weight, hereinafter the same), and more preferably within range of 0.1-65 %. In addition, every sort of synergists, antioxidant for improving stability, and other additives can be added as necessary in the insect control agent of this invention. Here, for preferred synergists, for example, piperonyl butoxide, isobornyl

thiocyanate, Lethane, and S-421 can be listed. For the antioxidant, butylhydroxyanisol, dibutyl hydroxy toluene, tocopherol, and γ -oryzanol can be listed for example. The amounts to add those additives are not limited, but it is appropriate to add them up to 10 times, normally 1/50-10 times the amount of the active ingredient compound. In addition, for another additive, for example, a subliming antibacterial agent/antifungal agent, such as p-chloro-m-~~xylenol~~ (PCMX), BCA, salicylic acid, benzoic acid, sorbic acid, 1-oxy-3-methyl-4-isopropylbenzene, O.P.P., and cypress thiol, can be listed. It is appropriate to add the subliming antibacterial agent/antifungal agent as another additive up to 70 %, preferably between 0.1 and 50 %. Furthermore, the insect control agent of this invention can be used mixing with a well known harmful insect control agent.

[0019]

Upon use, the insect control agent of this invention can be applied by placing in, spraying, coating, or adhering, being packaged or without packaging with appropriate packaging material, such as every sort of publicly known material, e.g. raising, crepe-like, net-like, layered, unwoven fabric, or fabric. Especially, since the active ingredient of this invention is substantially odor

free, it can be also applied so as to directly contact with clothes.

[0020]

In addition, the insect control agent for clothes according to this invention can be applied to a place of interest in a form being held by an appropriate sheet-type base material in advance, for example, by coating, impregnating, spraying, dripping, kneading, or the like. For the sheet-type base material used herein, for example, a synthetic resin sheet, such as polyethylene, polypropylene, nylon, polyvinyl chloride, polyvinylidene chloride, and polyester, animal or vegetable, or inorganic fiber sheet (paper, fabric, unwoven fabric, leather, etc.), a mixed material sheet or blend fabric of those synthetic resin and inorganic fiber or powder, blend fabric or unwoven fabric of the synthetic resin and animal or vegetable fiber, and a laminated sheet of those respective above-described sheets can be used.

[0021]

In addition, the harmful insect control agent of this invention can be used by being held by, for example, wood materials, such as paulownia, cedar, camphor tree, yew, fir, Sacharin fir, hemlock fir, jongkong, Jelutong, Agathis, Japanese cedar, Japanese walnut, beech, oak, zelkova,

Japanese elm, and Japanese cherry birch, plastics, such as vinyl chloride resin, chlorinated polyethylene, polyethylene, polypropylene, and vinyl chloride-vinyl acetate copolymer, cardboard, and so on by applying impregnating, dripping, kneading, and so on. For a suitable holding means herein, for example, a method, in which the active ingredient compound and liquid that gelatinizes, crystallizes, or solidifies at normal temperature are separately impregnated or mixed and then impregnated under normal pressure, reduced pressure, or increased pressure.

[0022]

For the liquid used herein, which gelatinizes at normal temperature, a common gelating agent, for example, dibenzylidene-D-sorbitol can be listed. For the liquid that crystallizes or solidifies at normal temperature, for example, acetanilide, dimethyl isophthalate, magnesium acetate, dimethyl terephthalate, maleic anhydride, lauric acid, stearyl alcohol, petroleum solid paraffin, animal or vegetable solid wax, sodium tetraborate (decahydrate), sodium aluminum sulfate, magnesium sulfate (hexahydrate), and disodium hydrogen phosphate (pentahydrate) can be listed.

[0023]

The harmful insect control agent of this invention, which is applied as described above, has strong effect, and appropriate degree of subliming property, and good stability. In addition, the effect can last for a few years in storage furniture, and when it is prepared in form of powder, granule, subliming agent, or the like, a small amount of the agent can be sublimed for short-term use. Furthermore, since the odor is hardly detected, it can be kept as odor free or desired odor can be added, and clothes kept in drawers for long time can be worn instantly after pulling out from the drawers. Therefore, it has many advantages, and is industrially highly valuable.

[0024]

[Effects]

The compound generally expressed by the above Formula (1) exhibits superior insect controlling effect against harmful insects for clothes. In addition, this compound exhibits a gasifying effect for longer period than conventional pirethroid compounds and has low toxicity, which is common with the pirethroid compounds.

[0025]

Hereunder, the invention will be fully described with Working Examples and Test Examples, but the present invention shall not be limited by those Working Examples.

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[0026] Working Example 1

Compound No.1 was applied to 3 mg/cm² on 20 mmφ x 3 mm pulp cardboard, and a mat-type insect control sheet was prepared.

Working Example 2

Using Compound No.2, 20 mmφ x 0.5 mm pulp cardboard was impregnated therein so as to be 3 mg/cm², and a mat-type insect control sheet was prepared.

Working Example 3

Using an acetone solution containing same parts by weight of Compound No.2 and Compound No.1, 20 mmφ x 0.5 mm pulp cardboard was impregnated so that the amount of the active ingredient is 1 mg/cm², and a mat-type insect control sheet was prepared.

[0027] Test Example 1

After impregnating filter paper having diameter of 20 mm so that the content of Compound 1 in each filter paper is as shown in Table 1 and then air-drying, each filter paper was hung in about 450 ml jar (made of glass) so as to

be about 8 cm above from the bottom. Then, a 90-mesh nylon gauze bag (4x4 cm) in which 10 of 30-day old clothes moths and one piece of 2x2 cm wool fabric were placed, was placed in the bottom of the container, and left in a dark place at 25 °C after sealing. After two weeks, the container was opened and the number of dead clothes moths was counted. The above-described test was performed twice and the results are shown as average dead insect rate in Table 1. Here, results of the same test performed with almost same concentration of empenethrin are also shown in Table 1 for comparison.

[0028]

[Table 1]

Table 1 Average Dead Insect Ratio

| Compound Name | Effective Compound Concentration (mg/sheet) | | |
|---------------|---|------|------|
| | 0.2 | 0.05 | 0.01 |
| Compound 1 | 100 | 100 | 50 |
| Empenthrin | 100 | 100 | 0 |

[0029]

[Effects of the Invention]

The harmful insect control agent according to this invention exhibits superior insect control effect against harmful insects for clothes, such as clothes moth and webbing clothes moths, in comparison with conventional pirethroid compounds, and is effective for long period at

suitable vapor pressure, and is superior agent that can be easily applied at household.

[AMENDMENT]

[FILING DATE] 20000402

[AMENDMENT 1] SPECIFICATION

[AMENDED ITEM(S)] WHOLE TEXTS

[METHOD OF AMENDMENT] CHANGES

[CONTENTS OF AMENDMENT]

[TYPE OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] INSECT CONTROL AGENT FOR
CLOTHES A STORAGE
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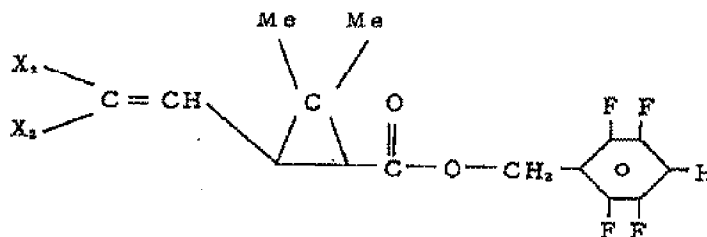
[FOREIGN TITLE] IRUIYO GAICHU BOJYOZAI
OYOBI SHUNOKAGU BUZAI

Claims

1. An insect control agent for clothes, which is featured by using a compound expressed by the following chemical formula (1) mixing with 1-ethynyl-2-methyl-2-pentenyl chrysanthemate:

Formula (1)

[Chemical Formula 1]

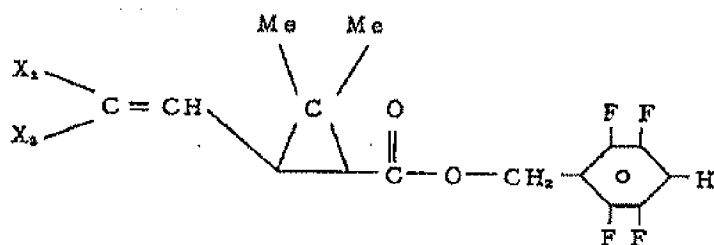


(where X_1 and X_2 are chlorine and/or methyl group).

2. An insect control agent for clothes, which is featured by using a compound generally expressed by the following formula (1) in form of a subliming solid agent by mixing with a subliming carrier.

Formula (1)

[Chemical Formula 2]



(where X_1 and X_2 are chlorine and/or methyl group)

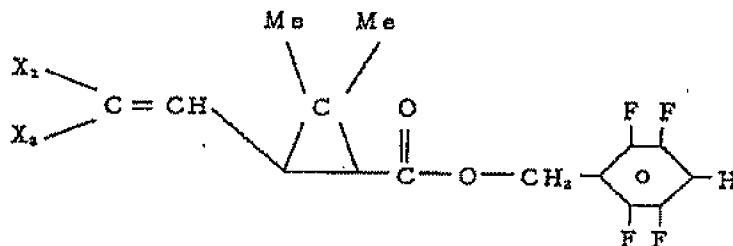
3. The insect control agent for clothes according to claim 2, wherein said subliming carrier is selected from a group consisting of tricyclodecane, cyclododecane, 2,4,6-triisopropyl-1,3,5-trioxane, trioxane, trimethylene norbornene, p-dichlorobenzene, naphthalene, and camphor.

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4. A storage furniture member, which is featured by holding a compound generally expressed by the following formula (1).

Formula (1)

[Chemical Formula 3]



(where X_1 and X_2 are chlorine and/or methyl group)

5. The storage furniture member according to claim 4, wherein said compound expressed by the formula (1) impregnates and is held said member.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a so-called "harmful insect control agent for clothes", and more specifically relates to a harmful insect control agent for clothes, which is effective for long period and is safe.

[0002]

[Conventional Technique]

Conventionally, for a harmful insect control agent for clothes, a control agent, such as p-dichlorobenzene, naphthalene, and camphor, has been widely used. These agents are to protect clothes by their subliming vapor by placing near clothes. Major effect of those insect control agents, however, is originally to repel harmful insects, and has characteristic odor. Therefore, this odor causes

odor transfer to clothes stored near the agents and generates uncomfortable feeling upon wearing, which is an issue to be solved in an insect control agent for clothes. Therefore, it has been recently studied to search for an insect control agent that is odor free and is effective by small amount.

[0003]

For an insect control agent that satisfies those conditions, only 1-ethynyl-2-methyl-2-pentenyl chrysanthemate (hereinafter referred to as "empenthrin") is known. Although this agent has high insecticidal activity against harmful insects, it hardly keeps the effect for long period. For use, every sort of slow-releasing methods (e.g. Unexamined Japan Patent Application Publication H2-196704) has been disclosed.

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harmful living organism, *Lepisma saccharina* for the order Thsanura; *Blatta orientalis*, *Periplaneta Americana*, *Leucophaea adela*, *Blattella germanica*, and *Acheta domestica* for the order Orthoptera; *Forficula Anisolabis* for earwigs; *Reticulitermes* for termites; *Pediculus humanus* for lice; *Cimex lectularius* Linnaeus, *Rhodnius prolixus*, and *Triatoma infectans* for the order Hemiptera; *Ephestia kuehniella* zeller and *Galleria mellonella* for the order Lepidoptera, *Anobium punctatum*, *Rhizopertha dominica*, *Hylotrupes bajulus*, *Oryzaephilus surinamensis*, *Sitophilus zeamais* Motschulsky, *Trogoderma* spp., *Anthrenus* spp., *Lyctus* spp., *Niptus hololeucus*, *Gibbium psylloides*, and *Tribolium* spp. for the order Coleoptera; *Monomorium pharaonis*, *Lasius niger*, and *Vespa* for the order Hemenoptera; *Aedes aegypti*, *Anopheles* spp., *Culex* spp., *Musca* spp., *Fannia* spp., *Calliphora* spp., *Lucilia* spp., *Chrysomyia* spp., *Stomoxys* spp., and *Tabanus* spp. for the order Diptera, *Xenopsylla* and *Ceratophyllus* spp. for the order Shiphonaptera are listed. However, effects against clothes moth and webbing clothes moth of the family Tineidae have not been known.

[0005]

[Problems to be Solved by the Invention]

For a harmful insect control agent for clothes, while it is required to have strong insect control effect against harmful insects for clothes and an insect damage preventing effect, it is also required to have low toxicity and last the above-described effects for long period. However, conventionally known harmful insect control agents for clothes, such as p-dichlorobenzene, naphthalene, and camphor, are inexpensive, and a large amount of them is used to make the effects last for long period. Accordingly, the toxicity is higher, and the effects are not satisfactory.

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On the other hand, a pirethroid compound, which has been known as a general insecticide for household use against flies, mosquitoes, and so on, has low toxicity. Especially empenethrin has been already used as a harmful insect control agent for clothes, but requires troublesome treatments for slow releasing, such as encapsulating in resin or a microcapsule, etc., which makes the agent expensive.

[0007]

For this reason, it has been demanded to find a compound that is effective for long period and has low toxicity and develop an effective harmful insect control agent for clothes.

[0008]

It is an object of the invention to provide a pirethroid-based harmful insect control agent for clothes, which exhibits superior insect control effect against harmful insects, especially clothes moth and webbing clothes moth, etc., and can keep the effects for long period.

[0009]

/7

[Means to Solve the Problems]

Inventors of this invention conducted thorough studies on an insect control effect of a number of pirethroid compounds, especially compounds known as pirethroid insecticides, against clothes moth and webbing clothes moth, which are representatives of harmful insects for clothes, and completed the invention.

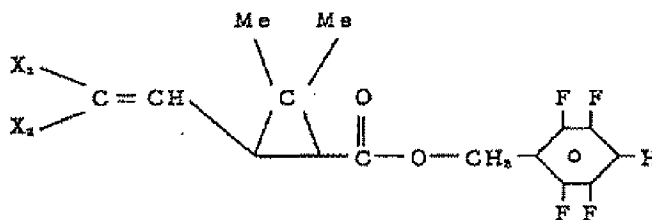
[0010]

More specifically, the present invention is a harmful insect control agent for clothes, which is featured by

containing as an active ingredient a compound generally expressed by the following chemical formula (1), and achieved the above object.

Formula (1)

[Chemical Formula 4]



(where X_1 and X_2 are chlorine and/or a methyl group.) In addition, the present invention achieved the above object by a harmful insect control agent for clothes, which is featured by mixing the compound expressed by the above formula (1) with a subliming carrier and using in a form of a subliming solid agent. Furthermore, the invention provides a storage furniture member, which is featured by holding the compound expressed by the above formula (1).

[0011]

In the compound, which is an active ingredient of the harmful insect control agent for clothes according to the invention and is generally expressed by the chemical formula (1), any of X_1 and X_2 can be chlorines or methyl groups, or one of them can be chlorine and the other can be

a methyl group, and even one of those compounds has many enantiomers and geometric isomers. Among them, 2,3,5,6-tetrafluorobenzyl (+)1R,3S-trans-2,2-dimethyl-3(2,2-dichlorovinyl)-cyclopropane carbonate (hereinafter, referred to as "Compound (1)") is preferred. In addition, 2,3,5,6-tetrafluorobenzyl (-)1R,cis/trans-2,2-dimethyl-3(2,2-dichlorovinyl)-cyclopropane carbonate and 2,3,5,6-tetrafluorobenzyl (±)1R,S-cis/trans-2,2-dimethyl-3(2-methyl-1-propenyl)-cyclopropane carbonate (hereinafter, referred to as "Compound (2)) can be also used.

[0012]

The harmful insect control agent for clothes according to this invention can exhibit superior control effect against harmful insects for clothes, and the compound generally expressed by the above formula (1) has appropriate vapor pressure, i.e. 2.7×10^{-4} mmHg/25 °C (obtained by extrapolation), which is almost halfway between vapor pressure of conventional highly subliming pirethroid compounds (normally on the order of $\times 10^{-3}$ mmHg/30 °C) and vapor pressure of common pirethroid compounds (normally on the order of $\times 10^{-5}$ mmHg/30 °C). Therefore, it can be fully expected to exhibit the gasifying effect and lasting effect at normal temperature, and has extraordinary performances such as substantially

odor free and extremely low toxicity. Especially for the effective insect control concentration of the compound generally expressed by the above formula (1) is, as in later-described test examples, base material impregnated in almost same amount of the agent as that of empenethrin that is already used as a harmful insect agent for clothes is more effective than empenethrin. Accordingly, it is more effective against harmful insects for clothes such as clothes moth and webbing clothes moth than empenethrin.

[0013]

Therefore, the compound generally expressed by the above formula (1) can exhibit satisfactory control effect by smaller amount than empenethrin, and can extend the active period at similar amount.

[0014]

The harmful insect control agent according to this invention can be also applied to a place where the agent is required to exhibit the insect control effects as is, for example, every sort of storage furniture used for storing clothes, such as Japanese-style chest, drawers, ordinary chest, and clothes box. However, it is normally prepared, for example, in solid form, such as powder, granule, tablet, stick, or sheet, or in liquid form, such as emulsifying agent, dispersant, aerosol agent, and oil solution, using

suitable carrier or excipient, and applied for controlling harmful insects for clothes by an appropriate method depending on the form of the agent.

[0015]

For the carrier (diluent) used for preparing the agent for liquid form, for example, water, alcohols such as ethyl alcohol, esters such as ethyl acetate, halogenated hydrocarbons such as dichloroethane, ketones such as acetone or methyl ethyl ketone, ethers such as tetrahydrofuran or dioxane, aliphatic hydrocarbons such as hexane, kerosene, paraffin, petroleum benzine, and aromatic hydrocarbons such as benzene and toluene can be used. In addition, for the liquid agent, common emulsifier, dispersant, spreading agent, wetting agent, stabilizer, spraying agent, and so on can be added/compounded. Furthermore, by compounding a normal film-forming agent, it can be made in a form of coating material, adhesive, and so on. For each additive used herein, for example, every sort of film-forming agents, such as cellulose derivatives such as nitrocellulose, acetyl cellulose, methyl cellulose, and acetyl butyl cellulose, vinyl resin such as vinyl acetate resin, alkyd resin, urea resin, epoxy resin, polyester resin, urethane resin, silicone resin, acrylic resin, rubber such as chlorinated rubber, and polyvinyl alcohol;

surfactants such as ether of polyoxyethylene fatty alcohol such as polyoxyethylene oleyl ether, polyoxyethylene alkyl allyl ether such as [polyoxyethylene nonylphenyl ether, ester of polyoxyethylene fatty acid, glyceride of fatty acid, sorbitan ester of fatty acid, sulfate ester of higher alcohol, alkyl allyl sulfonate salt such as sodium dodecylbenzene sulfonate; a spraying agent such as dimethyl ether or fluorocarbon; casein, gelatin, alginic acid, and carboxymethylcellulose (CMC) can be listed.

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[0016]

In addition, for a carrier used for preparing the agent in solid form, for a representative example, every sort of mineral substance powder such as silicic acid, kaolin, activated carbon, talc, calcium carbonate, and ceramic powder, every sort of vegetable substance powder such as wood powder, bean powder, flour, and starch, an inclusion compound such as cyclodextrin, and so on can be listed. Furthermore, for preparing the agent in a solid form, for example, using a subliming carrier, such as tricyclodecane, cyclododecane, 2,4,6-triisopropyl-1,3,5-trioxane, trioxane, trimethylene norbornene, p-dichlorobenzene, naphthalene, and camphor, the carrier and the compound generally expressed by the above formula (1)

can be mixed in melted condition or mixed in ground condition, and then can be molded to a subliming solid agent. In addition, the above-described solid agent can also include a form of a resin molded product, in which the active ingredient compound is kneaded in plastic.

[0017]

Furthermore, the harmful insect control agent for clothes according to this invention can be also prepared as in a micro-encapsulated form by a spray-dry ~~method~~ using polyvinyl alcohol, CMC, and so on, a hardening-in liquid method using gelatin, polyvinyl alcohol, alginic acid, and so on, or by coacervation method. In addition, it can be also included with cyclodextrin, or prepared in form of gel using gelating agent such as benzylidene-D-sorbitol and carrageenan.

[0018]

The insect control agent for clothes according to this invention, which is prepared in this way, can be any, and suitably determined according to each form, but normally contains the compound generally expressed by the above-described formula (1) preferably up to about 80 % (by weight, hereinafter the same), and more preferably within range of 0.1-65 %. In addition, every sort of synergists, antioxidant for improving stability, and other additives

can be added as necessary in the insect control agent of this invention. Here, for preferred synergists, for example, piperonyl butoxide, isobornyl thiocyanate, Lethane, and S-421 can be listed. For the antioxidant, butylhydroxyanisol, dibutyl hydroxy toluene, tocopherol, and γ -oryzanol can be listed for example. The amounts to add those additives are not limited, but it is appropriate to add them up to 10 times, normally 1/50-10 times the amount of the active ingredient compound. In addition, for another additive, for example, a subliming antibacterial agent/antifungal agent, such as p-chloro-m-~~xylenol~~ (PCMX), BCA, salicylic acid, benzoic acid, sorbic acid, 1-oxy-3-methyl-4-isopropylbenzene, O.P.P., and cypress thiol, can be listed. It is appropriate to add the subliming antibacterial agent/antifungal agent as another additive up to 70 %, preferably between 0.1 and 50 %. The insect control agent of this invention is preferably used by mixing the compound generally expressed by the above formula (1) with a well known harmful insect control agent.

[0019]

Upon use, the insect control agent of this invention can be applied by placing in, spraying, coating, or adhering, being packaged or without packaging with appropriate packaging material, such as every sort of

publicly known material, e.g. raising, crepe-like, net-like, layered, unwoven fabric, or fabric. Especially, since the compound generally expressed by the above formula (1) is substantially odor free, it can be also applied so as to directly contact with clothes.

[0020]

In addition, the insect control agent for clothes according to this invention can be applied to a place of interest in a form being held by an appropriate sheet-type base material in advance, for example, by coating, impregnating, spraying, dripping, kneading, or the like. For the sheet-type base material used herein, for example, a synthetic resin sheet, such as polyethylene, polypropylene, nylon, polyvinyl chloride, polyvinylidene chloride, and polyester, animal or vegetable, or inorganic fiber sheet (paper, fabric, unwoven fabric, leather, etc.), a mixed material sheet or blend fabric of those synthetic resin and inorganic fiber or powder, blend fabric or unwoven fabric of the synthetic resin and animal or vegetable fiber, and a laminated sheet of those respective above-described sheets can be used.

[0021]

In addition, the compound generally expressed by the above formula (1) can be used by being held by, for example,

wood materials, such as paulownia, cedar, camphor tree, yew, fir, Sacharin fir, hemlock fir, jongkong, Jelutong, Agathis, Japanese cedar, Japanese walnut, beech, oak, zelkova, Japanese elm, and Japanese cherry birch, plastics, such as vinyl chloride resin, chlorinated polyethylene, polyethylene, polypropylene, and vinyl chloride-vinyl acetate copolymer, cardboard, and so on by applying impregnating, dripping, kneading, and so on. For suitable holding means herein, for example, a method, in which the compound generally expressed by the above-described formula (1) and liquid that gelatinizes, crystallizes, or solidifies at normal temperature are separately impregnated or mixed and then impregnated under normal pressure, reduced pressure, or increased pressure.

[0022]

For the liquid used herein, which gelatinizes at normal temperature, a common gelating agent, for example, dibenzylidene-D-sorbitol can be listed. For the liquid that crystallizes or solidifies at normal temperature, for example, acetanilide, dimethyl isophthalate, magnesium acetate, dimethyl terephthalate, maleic anhydride, lauric acid, stearyl alcohol, petroleum solid paraffin, animal or vegetable solid wax, sodium tetraborate (decahydrate), sodium aluminum sulfate, magnesium sulfate (hexahydrate),

and disodium hydrogen phosphate (pentahydrate) can be listed.

[0023]

The harmful insect control agent of this invention, which is applied as described above, has strong effect, and appropriate degree of subliming property, and good stability. In addition, the effect can last for a few years in storage furniture, and when it is prepared in form of powder, granule, subliming agent, or the like, a small amount of the agent can be sublimed for short-term use. Furthermore, since the odor is hardly detected, it can be kept as odor free or desired odor can be added, and clothes kept in drawers for long time can be worn instantly after pulling out from the drawers. Therefore, it has many advantages, and is industrially highly valuable.

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[0024]

[Effects]

The compound generally expressed by the above Formula (1) exhibits superior insect controlling effect against harmful insects for clothes. In addition, this compound exhibits a gasifying effect for longer period than conventional pirethroid compounds and has low toxicity, which is common with the pirethroid compounds.

[0025]

Hereunder, the invention will be fully described with Reference Examples and Test Examples, but the present invention shall not be limited by those Reference Examples.

[0026] Reference Example 1

Compound No.1 was applied to 3 mg/cm² on 20 mmφ x 3 mm pulp cardboard, and a mat-type insect control sheet was prepared.

Reference Example 2

Using Compound No.2, 20 mm φ x 0.5 mm pulp cardboard was impregnated therein so as to be 3 mg/cm², and a mat-type insect control sheet was prepared.

Reference Example 3

Using an acetone solution containing same parts by weight of Compound No.2 and Compound No.1, 20 mmφ x 0.5 mm pulp cardboard was impregnated so that the amount of the active ingredient is 1 mg/cm², and a mat-type insect control sheet was prepared.

[0027] Test Example 1

After impregnating filter paper having diameter of 20 mm so that the content of Compound 1 in each filter paper is as shown in Table 1 and then air-drying, each filter paper was hung in about 450 ml jar (made of glass) so as to be about 8 cm above from the bottom. Then, a 90-mesh nylon

gauze bag (4x4 cm) in which 10 of 30-day old clothes moths and one piece of 2x2 cm wool fabric were placed, was placed in the bottom of the container, and left in a dark place at 25 °C after sealing. After two weeks, the container was opened and the number of dead clothes moths was counted. The above-described test was performed twice and the results are shown as average dead insect rate in Table 1. Here, results of the same test performed with almost same concentration of empenthrin are also shown in Table 1 for comparison.

[0028]

[Table 1]

Table 1 Average Dead Insect Ratio

| Compound Name | Effective Compound Concentration (mg/sheet) | | |
|---------------|---|------|------|
| | 0.2 | 0.05 | 0.01 |
| Compound 1 | 100 | 100 | 50 |
| Empenthrin | 100 | 100 | 0 |

[0029]

[Effects of the Invention]

According to this invention, by using by mixing with empenthrin, which is a conventional pirethroid-based insect control agent, or with a subliming carrier, or by being held in a store furniture member, the compound generally expressed by the formula (1) exhibits superior insect control effect against harmful insects for clothes, such as

clothes moth and webbing clothes moths, in comparison with conventional pirethroid compounds, and is effective for long period at suitable vapor pressure, and is superior agent that can be easily applied at household.
